Electrochemistry

Introduction:

Redox (oxidation-reduction) reactions will be used to determine the relative electrochemical reactivity of 5 metals. In Part I of the experiment, you will determine the activity ranking of these 5 metals from observing chemical reactions between the metals and metal nitrate solutions. Part II of the lab will involve constructing voltaic cells and measuring cell potentials using zinc as the standard electrode (instead of hydrogen). The standard reduction potential of zinc and the measured cell potentials will allow you to calculate the half-reaction potentials for the other 4 metals.

Part I: Electrochemical Activity from Chemical Reactions

Redox reactions involve the transfer of electrons from the substance oxidized to the substance reduced. An oxidation-reduction reaction occurs when a piece of aluminum metal is placed into a solution of copper(II) nitrate. The aluminum atoms lose three electrons and are oxidized to Al^{3+} ions, whereas the Cu^{2+} ions gain two electrons and are reduced to copper atoms. Hence, a coating of copper metal begins to form at the surface of the aluminum metal due to this electron transfer process.

In Part I of this experiment, you will look for similar evidence of reaction when you react five metals with their corresponding metal nitrate solutions. The results will allow you to arrange these five metals in order of increasing electrochemical activity.

Part II. Electrochemical activity from cell potentials

The redox reaction that takes place between aluminum metal and copper(II) nitrate is a single replacement reaction. The balanced molecular equation for this reaction can be written as follows:

$$2\ Al(s) + 3\ Cu(NO_3)_2(aq) \rightarrow 2\ Al(NO_3)_3(aq) + 3\ Cu(s)$$

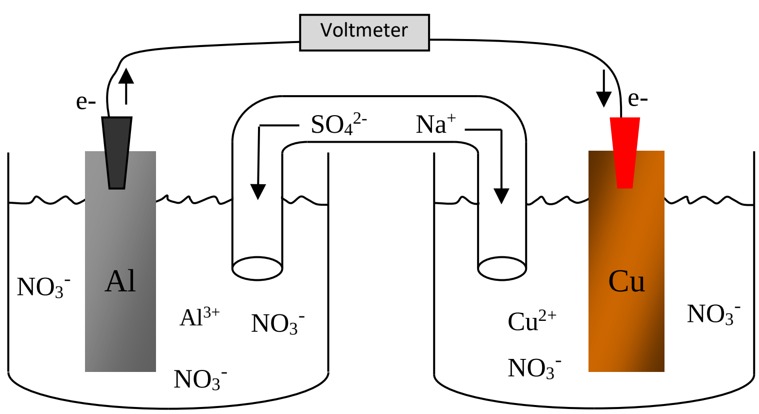
The net ionic equation for this reaction is: $2\ Al(s) + 3\ Cu^{2+}(aq) \rightarrow 2\ Al^{3+}(aq) + 3\ Cu(s)$

This reaction can also be broken down into an oxidation half-reaction and a reduction half-reaction as follows:

$$Al(s) \rightarrow Al^{3+}(aq) + 3\ e^- \qquad \text{oxidation half-reaction}$$

$$Cu^{2+}(aq) + 2\ e^- \rightarrow Cu(s) \qquad \text{reduction half-reaction}$$

These half-reactions can be separated by constructing a voltaic cell consisting of two half-cells as shown below.



Anode: $Al(s) \rightarrow Al^{3+} + 3e-$ Cathode: $Cu^{2+} + 2e- \rightarrow Cu(s)$

Each half-cell consists of a metal electrode immersed in a solution containing its corresponding cation. The electrode at which oxidation occurs is called the anode, and the electrode at which reduction occurs is called the cathode. The electrodes are connected by a wire through which electrons will flow from the anode to cathode to provide an electrical current. The half-cells are also connected by a salt bridge that permits the limited movement of ions into the two half-cells. This movement of ions completes the circuit and maintains the charge neutrality in each half-cell. For the voltaic cell shown above, negative ions from the salt bridge move into the anode half-cell as aluminum atoms are oxidized to form Al^{3+} ions. Positive ions from the salt bridge move into the cathode half-cell as Cu^{2+} ions are reduced to Cu(s).

The transfer of electrons takes place through the external wire because there is difference in electrical potential between the two electrodes that can be measured in volts. The cell potential is a measure of the tendency of the anode metal to be oxidized and the tendency of the metal ions in the cathode to be reduced. The standard cell potential, $E°_{cell}$, corresponds to 1 M solutions, gases at 1 atm pressure, and a temperature of 298 K.

Standard cell potentials can be considered to be the sum of the standard reduction potential for the cathode half reaction and the standard oxidation potential for the anode half reaction:

$$E°_{cell} = E°_{red} + E°_{ox}$$

In this equation, the oxidation potential for the anode reaction, $E°_{ox}$, is the negative of the reduction potential for the reverse reaction.

For example, if, $Zn^{2+}(aq) + 2e^- \rightarrow Zn(s)$ $\quad E°_{red} = -0.76$ V

Then $Zn(s) \rightarrow Zn^{2+}(aq) + 2e^-$ $\quad E°_{ox} = +0.76$ V

Thus, depending on whether Zn is the cathode or anode, we will use its respective reduction or oxidation potential and the measured cell potential, $E°_{cell}$, to find the half-cell potential for the other metal. The measured cell potential will also be used to calculate the standard free energy change, ΔG^o_{rxn}, and the equilibrium constant, K, using the equations provided below.

Equations to use for the calculations:

Cell potential: $E°_{cell} = E°_{red} + E°_{ox}$

$\Delta G^o_{rxn} = -nFE^o_{cell}$ where n = moles e^- transferred and F = 96,500 $\frac{J}{V \cdot mol\ e^-}$

$E^o_{cell} = \frac{RT}{nF} ln\ K$ where R = 8.314 J/mol·K and T = temperature in Kelvins

Materials:

Chromebook	1.0 M $AgNO_3$(aq)	5 strips of Zn(s)
GoLink	1.0 M $Cu(NO_3)_2$(aq)	2 strips of Mg(s)
Voltage probe leads	1.0 M $Zn(NO_3)_2$(aq)	2 strips of Pb(s)
laminated table	1.0 M $Mg(NO_3)_2$(aq)	2 strips of Cu(s)
di H_2O	1.0 M $Pb(NO_3)_2$(aq)	vial with 5 pieces of Ag(s)
forceps	1.0 M $NaNO_3$(aq)	wire cutters for metal strips
sandpaper	4 pieces of 2 inch string	50 mL beaker
well plate	scissors (for string)	10 mL beaker

Part I. Electrochemical Activity from Chemical Reactions

Warning: Be careful when handling $AgNO_3$(aq) – it will cause dark stains on your skin after it is exposed to sunlight. Make sure to wash your hands thoroughly before you leave the lab!

Note: You will check out the silver pieces from your instructor. Write your name on the sign out sheet. Do not put any of the Ag(s) pieces in the waste container! You must clean the silver pieces and return them to your instructor when you are finished with them!

1. Use sandpaper to briefly clean the surface of one strip each of copper, magnesium, and zinc to remove any oxide coatings. *Do not use sandpaper on the silver pieces*. **Cut the Cu, Mg, Pb, and Zn strips into four small pieces**. Place the pieces in the appropriate labeled boxes on the laminated reaction table. Also place the square silver pieces on the laminated table. Note: the rows refer to the solid metals, while the columns denote the aqueous metal nitrate solutions.

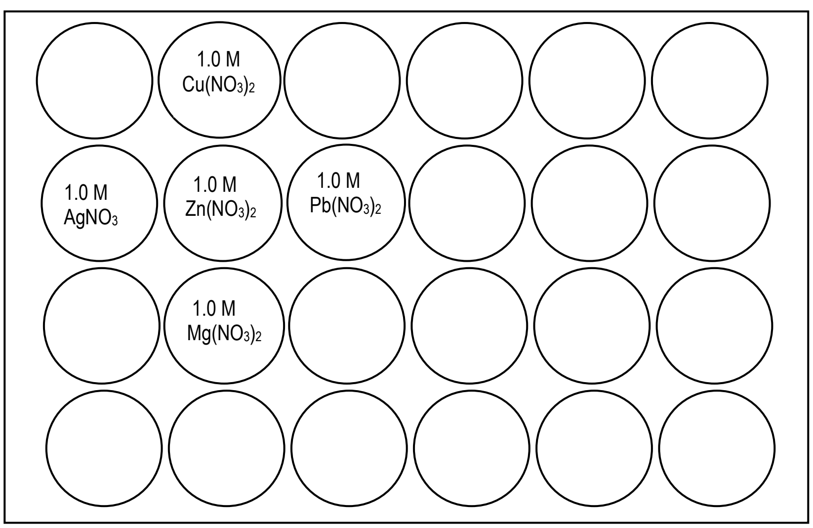
2. Place one drop of the appropriate aqueous metal nitrate solutions onto each piece of metal using the laminated table as your guide. For example, you will place one drop of $Cu(NO_3)_2$ on the Zn, Pb, Mg, and Ag pieces.
3. Allow the metal pieces and solutions to remain in contact for at least 15 minutes and proceed with Part II of this experiment. Record your observations in the data table for Part I. (Note: Examine the Mg and $Zn(NO_3)_2$ mixture carefully for evidence of a reaction and **see your instructor** to confirm.)
4. Have your instructor check your data table for Part 1 before you clean the laminated sheet!
5. **DO NOT PLACE THE SILVER PIECES IN THE WASTE CONTAINER! Use forceps to remove the Ag pieces from the laminated table**, place them in a small beaker and rinse with deionized water. Dry the silver pieces and return them to the original vial. Place the remainder of the metals and solutions in the waste container in the hood, rinse the laminated table with deionized water, and return the table to the special equipment container.

Part II. Electrochemical Activity from Cell Potentials

1. Obtain the Chromebook computer, GoLink system, and voltage probe leads.
2. View the following YouTube animation that shows the molecular-level processes occurring in a voltaic cell. Links can be found under the Electrochemistry activity on the CHM152LL web page.

   http://www.youtube.com/watch?feature=player_detailpage&v=C26pH8kC_Wk

3. Assemble the Chromebook, voltage probe leads, and GoLink system as directed in the "Using and calibrating a pH probe" technique. In the Vernier Graphical Analysis window, click the 3-square icon in the upper right corner to select "Meter." The units of cell potential displayed are volts (V).
4. When the voltage probe leads are not in contact with a cell (or each other), a meaningless default voltage may be displayed. If you touch the two leads together, the voltage should drop to 0.00 V (or close to 0.00 V). This will calibrate the leads. Also check to make sure that the metal pieces at the end of the leads do not appear corroded. (You may use sandpaper to clean them if they look black or rusted due to corrosion.)
5. Place enough $Zn(NO_3)_2$ solution in one of the center wells to fill it about one-half full, as shown in the figure below. Place about the same amount of 1.0 M $AgNO_3$ solution in an adjacent well.



6. Clean a piece of Zn ribbon with sandpaper, then bend the piece near the end. Remove the piece of Ag wire from the vial – do not try to clean the Ag with sandpaper! Use your results from Part I to predict which metal (Zn or Ag) is more active. Depending on which type of leads you have:

- **<u>Push-button style leads:</u>** Push the button on the end of the black lead to attach the black lead to the metal predicted to be more active. Attach the red lead to the metal that is predicted to be less active.
- **<u>Alligator clip style leads:</u>** Simply attach the black alligator clip lead to the metal predicted to be more active, and the red one to the metal predicted to be less active.

7. To prepare your salt bridge, place about 5-6 ml of 1.0 M $NaNO_3$ in a 10 ml beaker. Cut four pieces of string so that each piece is about two inchs long, and immerse the pieces of string in the $NaNO_3$ solution. Remove one piece of string, and place it so one end is inserted into the $Zn(NO_3)_2$ solution well and the other end is in the $AgNO_3$ solution well. **Immediately proceed to the next step.**

Note: Do not allow the metal clips on the black and red leads to come into contact with any solutions; this will corrode and eventually destroy the leads.

8. Insert the Zn electrode into the $Zn(NO_3)_2$ solution and the Ag electrode into the $AgNO_3$ solution, but make sure the black and red leads are not in direct contact with the solutions. After the reading has stabilized, record the voltage reading in the data table for Part II. The reading may fluctuate by about ± 0.01 V and the voltage will decrease with time, so it is important to record the voltage almost immediately after inserting the electrodes. (If the reading erratically fluctuates between (+) and (-) values, make sure there is good contact between the leads and metal electrodes, and that the black/red leads are not touching any solutions.)
9. If the cell voltage is ***positive***, as it should be for a spontaneous cell reaction, this indicates that the positive (red) lead is connected to the cathode, and the negative (black) lead is connected to the anode. If the cell voltage is ***negative***, this indicates that the leads are connected to the wrong metals. ***If the cell voltage is negative, switch the black and red leads with the metals.*** Once you get a positive voltage reading, record which metal is the anode and which is the cathode.
10. Remove the metal electrodes and the salt bridge from the well plate without contaminating the solutions in the wells, and disconnect the metal electrodes from the leads. Rinse the Ag wire electrode with deionized water and return it to the vial containing the silver pieces.
11. Place 1.0 M $Mg(NO_3)_2$ solution in a separate well that is adjacent to the $Zn(NO_3)_2$ reference well. Clean a new piece of Zn metal, and also clean a piece of Mg. Use a new salt bridge, and measure the Zn-Mg cell potential using the Zn and Mg electrodes. Record the potential in the data table for Part II. Also indicate which metal acts as the anode and which acts as the cathode. Disconnect the metal electrodes, and remove the salt bridge as soon as possible.
12. Check to see whether you need to add more $Zn(NO_3)_2$ solution to the reference cell to keep it one-half full. Then proceed in a similar way to measure the cell potentials of the Zn-Pb and Zn-Cu cells, making sure that you use clean metals and fresh salt bridges each time, and that you disconnect the electrodes and remove the salt bridge as soon as possible.
13. Check with your instructor that the cell potential readings are within an acceptable range. Do this before disassembling the Chromebook and cleaning the well plates. If the cell potential readings are not within acceptable limits, your instructor will tell you which readings must be redone. You should use fresh reagents, clean metals and a new salt bridge for any cells that you need to redo.

RETURN THE VIAL WITH THE SILVER PIECES TO YOUR INSTRUCTOR AND WRITE THE TIME RETURNED ON THE SIGN OUT SHEET. RETURN THE SPECIAL EQUIPMENT CONTAINER TO THE SHELVES BY THE INSTRUCTOR'S STATION.

Electrochemistry Pre-Lab Questions and Calculations

You will complete this quiz in Canvas 1 hour before your lab period. This page will not be turned in or graded. You may use this page to set up your calculations before you take the Canvas quiz.

1. Use the activity series below to determine if a reaction will happen between each pair of reactants. Select all that apply by placing an X on the line in front.
   Activity Series: (most active) Li > K > Ca > Na > Al > Zn > Fe > Co (least active)

   a) ____ Al (s) + $NaNO_3$ (aq) →

   b) ____ Ca (s) + $Fe(NO_3)_3$ (aq) →

   c) ____ Zn (s) + $Co(NO_3)_2$ (aq) →

   d) ____ Co (s) + $LiNO_3$ (aq) →

2. In lab, a voltaic cell is constructed in the following way: solid zinc is placed in a beaker containing a solution of $Zn(NO_3)_3$ (aq). Solid cobalt is placed in a beaker containing a solution of $Co(NO_3)_2$ (aq). The electrodes are connected to one another via a voltmeter. A salt bridge is used between the two beakers. Use the activity series above to determine which metal is the anode and which is the cathode.

   a. Within the voltaic cell, which metal would be at the anode? ______

   b. Which metal would be at the cathode? _____

   c. What is the half-reaction that occurs at the anode? _________________________

   d. What is the half-reactin that occurs at the cathode? ________________________

3. Select all answers that apply. In a voltaic cell, the most active metal is

   a) oxidized b) oxidizing agent c) cathode d) the metal attached to the black lead

4. If you obtain a negative reading for a voltaic cell during lab, what error was made?

5. Which metal pieces must be cleaned and returned to the instructor after use?

6. Which metal pieces must NOT be placed in the waste container?

7. Which chemical can cause dark stains on your hands?

8. If your voltage drops to 0, what is a possible error you made?

Name: ____________________________________ Experiment date: _____________

Electrochemistry Lab Report
Turn in pages 6 - 9 as your graded lab report.

Data: Table 1: Part I: Observations of solid metals in metal nitrate solutions. Write NR if no reaction takes place. (3 pts)

	Zn^{2+}*(aq)*	**Cu^{2+}*(aq)***	**Pb^{2+}*(aq)***	**Mg^{2+}*(aq)***	**Ag^{+}*(aq)***
Zn*(s)*					
Cu*(s)*					
Pb*(s)*					
Mg*(s)*					
Ag*(s)*					

Table 2: Part II. Measured Cell Potentials (4 pts)

		Anode Metal	**Cathode Metal**	**Measured Cell Potential, V**
#1	Zn-Ag			
#2	Zn-Mg			
#3	Zn-Pb			
#4	Zn-Cu			

Calculations: Instructor Initials: _________

1. For each voltaic cell, write each half reaction in the appropriate direction, then write the balanced net reaction for the cell. Calculate the half reaction potential of the other metal in each cell using the standard reduction potential of Zn^{2+} (E^o_{red} = -0.76 V) and the measured cell potential (E^o_{cell}).

<u>Voltaic Cell #1: Zn and Ag</u> Use your measured cell potential for E^o_{cell}. Given Zn^{2+}*(aq)* + $2e^-$ $\rightarrow$ Zn*(s)*, E^o_{red} = -0.76 V, calculate the potential for the other half reaction. (3 pts)

A. half reaction in the anode: ________________________________ E^o_{ox} = __________

B. half reaction in the cathode: ______________________________ E^o_{red} = __________

C. Balanced cell reaction: ____ E^o_{cell} = ________

<u>Voltaic Cell #2: Zn and Mg</u> Use your measured cell potential for E^o_{cell}. Given Zn^{2+}*(aq)* + $2e^-$ $\rightarrow$ Zn*(s)*, E^o_{red} = -0.76 V, calculate the potential for the other half reaction. (3 pts)

A. half reaction in the anode: ________________________________ E^o_{ox} = __________

B. half reaction in the cathode: ______________________________ E^o_{red} = __________

C. Balanced cell reaction: ____ E^o_{cell} = _______

Voltaic Cell #3: Zn and Pb Use your measured cell potential for E^o_{cell}. Given Zn^{2+}*(aq)* + $2e^-$ $\rightarrow$ Zn*(s)*, E^o_{red} = -0.76 V, calculate the potential for the other half reaction. (3 pts)

A. half reaction in the anode: ________________________________ E^o_{ox} = __________

B. half reaction in the cathode: ______________________________ E^o_{red} = __________

C. Balanced cell reaction: ____ E^o_{cell} = ________

Voltaic Cell #4: Zn and Cu Use your measured cell potential for E^o_{cell}. Given Zn^{2+}*(aq)* + $2e^-$ $\rightarrow$ Zn*(s)*, E^o_{red} = -0.76 V, calculate the potential for the other half reaction. (3 pts)

A. half reaction in the anode: ________________________________ E^o_{ox} = __________

B. half reaction in the cathode: ______________________________ E^o_{red} = __________

C. Balanced cell reaction: ____ E^o_{cell} = _______

2. Show a sample calculation of ΔG^o for the Zn-Ag cell. Write the calculated ΔG^o values for all 4 cells in table 3 on page 8. (2 pts)

3. Show a sample calculation for the equilibrium constant, K, for the Zn-Ag cell. Assume T = 298 K. Write the calculated K values for all 4 cells in table 3 on page 8. (2 pts)

Instructor Initials: _________

Results:

Part I:

1. Place the **metals** Zn(s), Cu(s), Pb(s), Mg(s), and Ag(s) in order of **decreasing** electrochemical activity based on your observations from the chemical reactions. (2 pts)

A. ________ B. ________ C. ________ D. ________ E. ________
most active least active

2. Write correctly **balanced** net ionic reactions for the following selected combinations based on your results for Part I. If there was no reaction simply write NR. (4 pts)

a. _____ $Zn^{2+}(aq)$ + _____ $Cu(s)$ → ____

b. _____ $Ag^{+}(aq)$ + _____ $Zn(s)$ → ____

c. _____ $Cu^{2+}(aq)$ + _____ $Mg(s)$ → ____

d. _____ $Ag^{+}(aq)$ + _____ $Cu(s)$ → ____

Part II:

Table 3. Results Table (6 pts)

Cell		**$E°_{cell}$ (V)**	**ΔG° (kJ)**	**K**
#1	Zn-Ag			
#2	Zn-Mg			
#3	Zn-Pb			
#4	Zn-Cu			

Table 4. Reduction Half Reactions and Experimental Reduction potentials (4 pts)

Write the appropriate reduction half-reaction for each metal ion in the table below and fill in the $E°_{red}$ value that you *calculated on pages 6-7*.

Reduction Half-Reaction Equation		**$E°_{red}$ values from experiment**	**$E°_{red}$ values from textbook for comparison**
Zn^{2+}	Ex. $Zn^{2+}(aq) + 2e^- \rightarrow Zn(s)$	-0.76 V	-0.76 V
Ag^{+}			0.80 V
Mg^{2+}			-2.37 V
Pb^{2+}			-0.13 V
Cu^{2+}			0.34 V

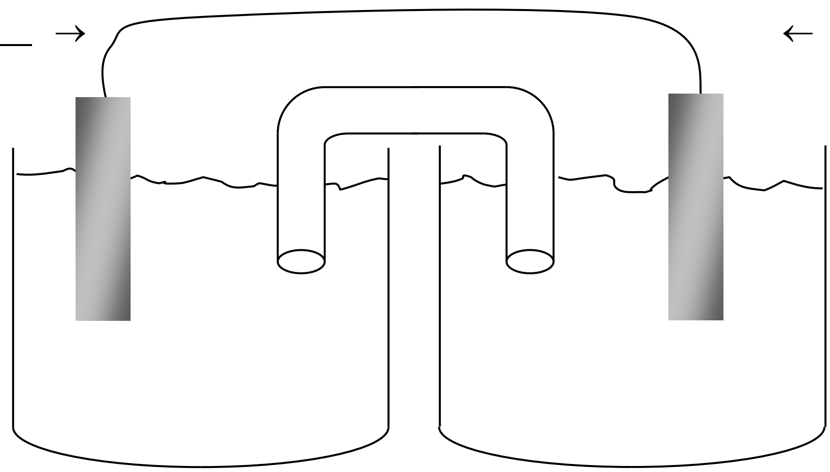
1. (2 pts) Place the **metals** Zn(s), Cu(s), Pb(s), Mg(s), and Ag(s) in order of decreasing electrochemical activity based on the experimental reduction potentials. (***Hint:*** The more active metal is easier to oxidize.)

A. _________ B. _________ C. _________ D. _________ E. _________
most active least active

2. (4 pts) Drawing of Voltaic Cell #3: Zn - Pb cell: Label the following:

   a. Anode metal, anode solution, and half reaction in the anode compartment.
   b. Cathode metal, cathode solution, and half reaction in the cathode compartment.
   c. The direction of electron flow.
   d. Using $NaNO_3$ as the salt bridge, the direction of ion flow in the salt bridge.

Anode = ____ → ← ____ = Cathode



Anode half reaction: ___________________ Cathode half reaction: ___________________

Conclusion: Summarize and compare the electrochemical activity of the five metals for both parts of the activity. Also summarize the trends in values (as E^o_{cell} increases, what happens to ΔG^o and K)? (5 pts)

Post-Lab Questions:

These questions will not be graded as part of your lab report grade. You will be responsible for the information in these questions and able to answer these or similar questions on the final exam.

1. As the **cell potential <u>decreases</u>**:

   The standard Gibb's free energy ↑ or ↓ _____

   K ↑ or ↓ _____

2. Identify whether each process occurs at the **cathode or anode** for a voltaic cell. You may want to view the YouTube electrochemical cell animations again to answer these questions.

   a. Metal atoms are oxidized. _______________

   b. Metal ions are reduced. ________________

   c. Anions from the salt bridge move towards _______________

   d. The less active metal is the _______________

   e. The mass of the ____________ increases.

   f. The concentration of the metal ions increases. ____________

   g. Electrons move from _______________ to _______________

3. Metals are **oxidized** into metal cations as they lose electrons and their charge increases. Thus metals are reducing agents. Metal cations are **reduced** to metal elements (solids except for Hg) as they gain electrons and their charge is reduced to zero. Thus metal cations are oxidizing agents. Answer the following questions about solid Zn, Cu, Pb, Mg, and Ag and their corresponding aqueous ions. Make sure to include (s) or (aq).

   a. Which is easiest to oxidize? ________

   b. Which is hardest to oxidize? ________

   c. Which is easiest to reduce? ________

   d. Which is hardest to reduce? ________

   e. Which is the best reducing agent? ________

   f. Which is the best oxidizing agent? ________

4. Assign oxidation numbers for all of the elements in the following redox reaction from a common voltaic cell.

   $Zn(s) + 2MnO_2(s) + 2NH_4^+(aq) \rightarrow Zn^{2+}(aq) + Mn_2O_3(s) + 2NH_3(aq) + H_2O(l)$ **<u>dry cell battery</u>**

   Element that is oxidized: ______ Element that is reduced: ______

   Oxidizing agent: ____________ Reducing agent: ____________

5. Discuss at least 2 experimental sources of error and how they affected your results.